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(54) POLYMERIZATION INHIBITION

(71) We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, Unites Sttaes of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly desvribed in and by the following statement:—

The invention concerns the inhibition of the polymerization of acrylate salts or methacrylate salts in aqueous solution.

Acrylate and methacrylate esters are well known, and their preparation has been amply disclosed in the literature and the art. One process for the preparation of acrylate and methacrylate esters involves obtaining, at an intermediate stage in the process, a stream containing about 2 to 3% of acrylic or methacylic acid. The acrylic or methacrylate acid in this stream is present in sufficiently large amounts to justify recovering such acids and recycling them as part of the feed stream. As part of the process for recovering the acrylic or methacrylic acid values, the intermediate stream containing such acid is neutralized with ammonia or other suitable aqueous base to obtain an acid-free organic layer and an aqueous acrylate or methacrylate salt layer.

It is this aqueous acrylate or methacrylate salt layer which tends to cause problems. The aqueous acrylate or methacrylate salt layer is particularly prone to polymerization. This polymerization will not only result in loss of the acrylic or methacrylic acid values, but may also result in the fouling of the equipment. The heretofore known polymerization inhibitors have been found to be ineffective in preventing the polymerization of the aqueous acrylate or methacrylate salt layer.

The present invention provides an aqueous solution of an acrylate salt or a methacrylate salt, said solution having a pH from 6 to 13 and containing a polymerization inhibiting amount of a nitrosophenolate or a substituted nitrosophenolate.

The present invention also provides a method for inhibiting the polymerization of an acrylate salt or a methacrylate salt in an aqueous solution which is at ambient temperature or above and has a pH from 6 to 13, said method comprising contacting said salt with a polymerization inhibiting amount of a nitrosophenolate or a substituted nitrosophenolate.

Any nitrosophenolate or substituted nitrosophenolate can be used which is water-soluble. The nitrosophenolate may be an alkali earth metal salt (such as lithium, sodium, potassium or cesium), an alkaline earth metal salt (such as calcium or barium), and ammonium salt or an alkyl substituted ammonium salt (such as a tetramethyl ammonium salt, diethyl ammonium salt or cetylammonium salt).

The substituted nitrosophenolates which can be used are those where the substitution will not sterically hinder the phenolate group. Thus, such substituted nitrosophenolates may be used which has a chlorosubstitution, an alkyl substitution such as a decyl substitution, an alkyl chloro substitution, a fused aromatic substitution such as is found in a nitrosoquinoline, a sulfonate substitution and an alkoxy substitution such as a methoxy group.

The nitrosophenolate or substituted nitrosophenolate will usually have the nitroso group para or ortho to the phenolate group.

Among the nitrosophenolates and substituted nitrosophenolates which may be used are:

The ammonium salt of

4-nitroso-2-chlorophenolate
5-methoxy-2-nitrosophenolate
8-hydroxy-5-nitrosoquinoline
6-chloro-3-nitroso-2-methylphenolate
p-nitrosophenolate
1-nitroso-2-naphtholate.
The sodium salt of
p-nitrosophenolate
1-nitroso-2-naphthol-3,6-disulfonate.

The nitrosophenolate or substituted nitroso-

phenolate are usually used in an amount of from 10 parts per million to 5,000 parts per million based on the weight of the aqueous acrylate or methacrylate solution and preferably in an amount of from 100 to 500 parts per million. Although amounts in excess of 5,000 parts per million may be used, there is no advantage in using such a large excess and there is the attendant economic disadvantage of using larger amounts of the nitrosophenolate or substituted nitrosophenolate than is necessary.

The pH of the acrylate or methacrylate salt solution is preferably from 8 to 11.

If the pH of the acrylate or methacrylate salt solution falls below 6, then the acrylate or methacrylate salt will be converted to the free acid. Additionally, at a pH of below 6, the nitrosophenolate or substituted nitrosophenolate will not exist as a salt.

Although this invention is useful with an acrylate or methacrylate salt whose concentration in the aqueous solution is less than 1% by weight, the invention is most preferably applied to such salts having a concentration above about 1%. If the concentration of the acrylate or methacrylate salt is less than 1%, then it is economically unfeasible to recover the acrylic or methacrylic acid values. However, even at concentrations below about 1%, the invention is useful in that the composition and process of this invention prevents the polymerization of the acrylate or methacrylate salt and the attendant buildup of polymer solids on the equipment which eventually will force the shutdown of such equipment servicing.

The temperatures of the acrylate or methacrylate salt solution to which this invention applies may vary widely from above freezing to below the boiling point. It is preferred, however, that the temperature of such acrylate or methacrylate salt solution be ambient temperature or slightly above 30°C. As a practical matter, the temperature of the acrylate or methacrylate solution will be that temperature at which the process stream happens to be at the time of treatment.

In a particularly preferred embodiment of this invention, a chelating agent is present to counter the effect of metal ions which are often present during processing. These metal ions participate in redox reactions which can generate polymerization initiators.

The amount of the chelating agent will vary from 1 to 500 parts per million based on the total weight of the aqueous acrylate or methacrylate solution and preferably from 10 to 100 parts per million. Amounts of chelating agent which are below one part per million are ineffective. Although the amount of chelating agent may exceed 500 parts per million, there is no particular advantage in using such a large amount. The chelating agent of choice in practicing this invention is ethylene diamine tetraacetic acid although other chelating agents may also be used which act similarly to the ethylene diamine tetraacetic acid.

In order to more fully illustrate the nature of this invention and the manner of practising the same, the following examples are presented.

EXAMPLES.

Distilled, uninhibited acrylic acid is slowly added to a flask containing a 50% excess (of the amount required to neutralize the acrylic acid) of 20% aqueous ammonia cooled in ice. The resultant solution is cooled to 25°C., and is then saturated with air at that temperature. Tertiary butyl hydroperoxide (490 parts per million) and Fe^{+2} (0.04 parts per million; added as ferrous sulfate) is added and the solution is placed in one ounce vials in which the aqueous ammoniacal solution of inhibitor candidates are previously placed with a glass bead for use in agitation. The vials are then capped in such a way as to exclude any air space. The samples are then shaken and allowed to sit at room temperature in a dim light and are visually observed. The induction period to the first appearance of any turbidity is measured in minutes and is set forth in Table I.

The example is repeated several times using different concentrations of inhibitors, a different initiating system (sodium persulfate, 200 ppm and sodium bisulfite adduct of formaldehyde, 200 ppm), and a caustic solution (50% excess) in place of the ammoniacal solution used above. The results are expressed in Table I.

TABLE I

Induction Times (minutes) for Initiated Polymerizations of 45% (by weight) Aqueous Ammonium or Sodium Acrylate at 25°C.

Polymerization Initiator System	Tertiary butyl hydroperoxide/Fe^{+2}			Sodium Persulfate/Sodium Bisulfate Adduct of Formaldehyde		
Inhibitor Concentration (Moles/Liter of Acrylate Solution)	10^{-3}	10^{-4}	None[1]	10^{-3}	10^{-4}	None[1]
Inhibitor						
4-nitroso-2-chlorophenolate(NH_4^+)	7200	216	18	*	49	29
5-methoxy-2-nitrosophenolate(NH_4^+)	2940	50	21	4400	5600	40
8-hydroxy-5-nitrosoquinoline(NH_4^+)	1800	*	21	248	112	40
6-chloro-4-nitroso-2-methylphenolate(NH_4^+)	693	105	21	58	*	29
p-nitrosophenolate(NH_4^+)	1380	*	46	396	*	40
p-nitrosophenolate(Na^+)	1700	*	17	20250	105	81
1-nitroso-2-naphtholate(NH_4^+)	708	360	59	127	119	41
1-nitroso-2-naphthol-3,6-disulfonate(Na^+)	99	82	33	115	*	24

[1] The variation in induction times is attributable to the fact that the experiments were performed, in some cases, on different batches of acrylate solution.

* Indicates that no statistically significant increase in the induction time was observed.

WHAT WE CLAIM IS:—

1. An aqueous solution of an acrylate salt or a methacrylate salt, said solution having a pH from 6 to 13 and containing a polymerization inhibiting amount of a nitrosophenolate or a substituted nitrosophenolate.

2. An aqueous solution according to Claim 1, wherein said nitrosophenoate or substituted nitrosophenolate is present in an amount of from 10 to 5000 parts per million based on the weight of the aqueous acrylate or methacrylate salt solution.

3. A solution according to Claim 1 or 2, wherein the nitrosophenolate or substituted nitrosophenolate has the nitroso group para or ortho to the phenolate group.

4. An aqueous solution according to any one of Claims 1 to 3, wherein said salt is ammonium acrylate.

5. An aqueous solution according to any one of Claims 1 to 4, wherein said nitrosophenolate is sodium p-nitrosophenolate.

6. An aqueous solution according to any preceding claim, wherein a chelating agent is present in an amount of from 1 to 500 parts per million based on the weight of the aqueous acrylate or methacrylate solution.

7. An aqueous solution according to Claim 6, wherein said chelating agent is ethylene diamine tetraacetic acid.

8. A method for inhibiting the polymerization of an acrylate salt or a methacrylate salt in an aqueous solution which is at ambient temperature or above and has a pH from 6 to 13, said method comprising contacting said salt with a polymerization inhibiting amount of a nitrosophenolate or a substituted nitrosophenolate.

9. A method according to Claim 8, wherein said nitrosophenolate or substituted nitrosophenolate is present in an amount of from 10 to 5000 parts per million, based on the weight of the aqueous acrylate or methacrylate solution.

10. A method according to Claim 8 or 9, wherein the nitrosophenolate or substituted nitrosophenolate has the nitroso group para or ortho to the phenolate group.

11. A method according to any one of Claims 8 to 10, wherein said salt is ammonium acrylate.

12. A method according to any one of Claims 8 to 11, wherein said nitrosophenolate is sodium p-nitrosophenolate.

13. A method according to any one of Claims 8 to 12, wherein a chelating agent is present in an amount of from 1 to 500 parts per million based on the weight of the aqueous acrylate or methacrylate salt solution.

14. A method according to Claim 13, wherein said chelating agent is ethylene diamine tetraacetic acid.

15. A method according to any one of Claims 8 to 14, wherein said aqueous solution has a pH of from 8 to 11.

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